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KINETIC STUDY ON HYDROCARBON FORMING PYROLYSIS OF FUSHUN AND MAOMING OIL SHALES

By

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INTRODUCTION

There are many different experimental techniques for studying the pyrolysis kinetics of oil shale. The differential thermal analysis (DTA) method is based on the change in the quantity of heat absorbed and the thermogravimetric (TGA) method, on the loss of the sample weight accompanying the heating of oil shale sample (1, 2). However, by using these methods, when kerogen is pyrolyzed by heating, the mineral matter contained in oil shale will also be decomposed, with heat liberation and weight loss, which affects the kinetic parameter study. The main purpose of the oil shale retorting is to produce shale oil and hydrocarbon gases, so it is necessary to study the hydrocarbon forming pyrolysis of oil shale. Some researchers designed special apparatus for this purpose (3).

In this paper, "Rock Eval." pyrolysis apparatus is used for studying hydrocarbon forming pyrolysis kinetics. In general, this apparatus has been designed and used only for evaluation of source rocks, not for kinetic studies.

EXPERIMENTAL

The apparatus used is called "Rock-Eval", Type I, designed by I. F. P. and manufactured by Gridal Corp., in France. It is shown schematically in literature (4). A 100-mg sample with the size of less than 80 mesh is heated with constant rate to about 550°C. During heating, inert gas is passed through the sample layer in order to carry out the gaseous product evolved. The hydrocarbons already present in the sample in a free or adsorbed state are first volatilized at a moderate temperature. The amount of these hydrocarbons (S_1) is measured by a flame ionization detector (FID) which eliminates the interference of mineral matter decomposition. Then, pyrolysis of kerogen results in generating hydrocarbons and hydrocarbon-like compounds (S_2) and oxygen-containing volatiles, i.e., carbon dioxide (S_3) and water. The volatile compounds generated are split into two streams passing respectively through a FID (detector) measuring S_2 and a thermal conductivity detector measuring S_3. An adequate temperature program allows a good separation of S_1 and S_2 peaks on the FID detector. In this paper, we are interested in the amount of the hydrocarbons (S_2) generated.

The experimental conditions used in this study are as follows: carrier gas is helium; constant heating rate is 5°C per minute.

Four Chinese oil shale samples are used: Fushun oil shale with rich kerogen content; Fushun oil shale with lean kerogen content; Maoming Jin Tang oil shale; and Maoming Yang Jiao oil shale.

RESULTS

Evaluation data of the samples are shown in Table I.

Kinetic data are shown in Tables II-V. In these tables, S_i means the sum of the integrated area indicating the sum of the amounts of pyrolysis hydrocarbon obtained from the beginning of the experiment to certain definite time, (or temperature); S_{∞} means the total amount of the integrated area, indicating the total amount of the hydrocarbon obtained in the whole run; and $x_i\% = S_i/S$ indicates the percentage of the hydrocarbon obtained from the beginning to the time t_i sec. (or T_i°C).

The data obtained are treated by using the kinetic equation of overall first order reaction,

$$\frac{dx}{dt} = Ae^{-E/RT}(1-x) \qquad 1)$$

TABLE I

EVALUATION DATA OF FUSHUN AND MAOMING OIL SHALE

Oil Shale	Organic Carbon	Adsorbed Hydrocarbon	Pyrolysis Hydrocarbon	CO_2 Content
	COT Wt %	S_1 mg/gm	S_2 mg/gm	S_3 mg/gm
Fushun (rich)	18.92	1.98	204.71	0.71
Fushun (lean)	9.28	0.82	87.67	0.39
Maoming Jin Tang	20.15	1.35	158.09	2.11
Maoming Yang Jiao	22.29	2.14	135.24	5.49

TABLE II

PYROLYSIS DATA OF FUSHUN RICH OIL SHALE

Time sec.	Temp. °C	S_i	x_i %
480	287	52	0.15
600	298	110	0.32
720	308	171	0.50
840	319	247	0.72
960	330	343	1.00
1080	340	506	1.47
1200	351	792	2.31
1320	361	1324	3.86
1440	372	2342	6.82
1560	383	4359	12.69
1680	393	8981	26.15
1800	404	16364	47.65
1920	414	25089	73.06
2040	425	31519	91.38
2160	436	33601	97.85
2280	446	33964	98.90
2400	457	34102	99.30
		S_α 34341	100.00

For constant heating rate, i.e., dt=dT/C, Equation 1 can be rewritten in logarithmic form:

$$\log\left[\frac{dx}{(1-x)dT}\right] = \log\frac{A}{C} - \frac{E}{2.303R}\cdot\frac{1}{T} \qquad 2)$$

where C: heating rate, 0.0833°C/sec. in this work;
R: 1.987 cal/mol K;
E: apparent activation energy, cal/mol;
A: apparent frequency factor, 1/sec;
x: percentage of hydrocarbon formed from beginning to a certain temp.
T: pyrolysis temperature, K.

By assuming $\Delta x/\Delta T = dx/dT$, from the data given in Tables II-V, a series of different sets of $1/T_i$ and

$$\log\left[\frac{x_i}{(1-x_i)T_i}\right]$$

at different T_i is calculated. From these values, an interative regression analysis allows the calculation of the slope $-E/2.303R$ and intercept $\log A/C$ of Equation 2. Then E and A can be obtained, which are given in Table VI.

TABLE III

PYROLYSIS DATA OF FUSHUN LEAN OIL SHALE

Time sec.	Temp. °C	S_i	x_i %
540	300	66	0.29
660	310	135	0.59
780	320	214	0.94
900	330	341	1.34
1020	340	418	1.84
1140	350	582	2.56
1260	360	838	3.69
1380	370	1259	5.54
1500	380	2025	8.91
1620	390	3500	15.40
1740	400	5648	24.90
1860	410	9117	40.10
1980	420	14100	62.10
2100	430	18970	83.50
2220	440	20954	92.20
2340	450	22298	98.10
2460	460	22510	99.10
		S_∞ 22723	100.00

TABLE IV

PYROLYSIS DATA OF MAOMING JIN TANG OIL SHALE

Time sec.	Temp. °C	S_i	x_i %
420	282	588	1.07
540	292	677	1.23
660	302	790	1.43
780	312	952	1.73
900	322	1195	2.17
1020	332	1595	2.89
1140	342	2226	4.04
1260	352	3249	5.90
1380	362	5000	9.08
1500	372	8003	14.53
1620	382	12964	23.53
1740	392	20400	37.04
1860	402	30340	55.09
1980	412	40052	72.72
2100	422	48561	88.17
2220	432	52246	94.86
2340	442	53717	97.53
2460	452	54357	98.69
		S_α 55078	100.0

The reaction rate constant k at a definite temperature may be calculated by using Equation 3:

$$K = Ae^{-E/RT} \qquad 3)$$

The time required for pyrolysis at constant pyrolysis temperature can be calculated by using Equation 4:

$$t = \frac{1}{k} \ln (1-x) \qquad 4)$$

Both results are shown in Table VII.

TABLE V

PYROLYSIS DATA OF MAOMING YANG JIAO OIL SHALE

Time sec.	Temp. °C	S_i	x_i %
480		119	0.53
600		303	1.34
720		538	2.37
840		928	4.10
960		1388	6.10
1080		2201	9.72
1200		3186	14.06
1320		4761	21.02
1440		6678	29.45
1560		9178	40.52
1680		13125	57.94
1800		17031	75.18
1920		19757	87.22
2042		21275	93.92
2160		21840	96.41
2280		22136	97.18
2400		22310	98.48
		S_∞ 22653	100.0

TABLE VI

APPARENT ACTIVATION ENERGY AND APPARENT FREQUENCY FACTOR

Oil Shale	% of H.C. produced x %	Apparent Activation Energy E Kcal/mol	Apparent Frequency Factor A 1/sec	Correlation Factor r
Fushun (rich)	0.7-97.9	55.72	3.21×10^{15}	0.989
Fushun (lean)	1.2-90.6	47.63	3.98×10^{12}	0.988
Maoming Jin Tang	1-93	38.76	9.35×10^{9}	0.990
Maoming Yang Jiao	0.5-94	31.20	4.67×10^{7}	0.993

CONCLUSIONS

It is feasible to use the Rock Eval apparatus for studying hydrocarbon-forming kinetics of oil shales. Four Chinese oil shale samples are used. Under experimental conditions, the main stage of hydrocarbon formation during pyrolysis may be treated as an overall first order kinetic model. The experimental data are well fitted with the kinetic equations obtained with calculated apparent activation energy and frequency factor. The time required for pyrolysis under constant temperature are also calculated. These results may be used for the design of the pyrolysis retort, especially for fine particles of oil shales.

TABLE VII

REACTION CONSTANT AND PYROLYSIS TIME REQUIRED AT CONSTANT TEMPERATURE

Oil Shale	Pyrolysis Temp. T °C	Reaction Rate Constant K 1/sec.	Pyrolysis Time required for x=95% sec.	Pyrolysis Time required for x=98% sec.
Fushun (rich)	400	0.00257	1165	1522
	425	0.0114	262	343
	450	0.0459	65	85
Fushun (lean)	400	0.00135	2218	2898
	425	0.00485	617	807
	450	0.0159	188	246
Maoming Jin Tang	400	0.0024	1247	1630
	425	0.0068	440	675
	450	0.0171	167	218
Maoming Yan Jiao	400	0.00344	870	1137
	425	0.00794	377	492
	450	0.017	176	230

LITERATURE CITED

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